

Highly efficient nano-tips with metal – dielectric coatings for tip-enhanced spectroscopy applications

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Abstract

We studied how a protection layer influences the performance of an Ag-coated dielectric tip in tip-enhanced Raman spectroscopy using 3D simulations. Two typical chemically inert materials, Au and SiO₂ were considered in this work. Neither of them introduces a significant shift of the resonance frequency; the field enhancement as well as the spatial resolution can also be preserved with a thin protective layer. Surprisingly, a 5 nm layer of SiO₂ can even improve the field enhancement of the tip. This provides a new method to prevent Ag tips from undesired physical and chemical damages without losing their original performance for TERS.

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The design and fabrication of robust and high performance tips is the key problem for tip-enhanced Raman spectroscopy (TERS), a novel methodology allowing nano-scale chemical analysis with single molecule sensitivity [1–3]. In TERS, two types of tips are commonly used so far, namely, conical tips made of etched metal wires and metal-coated atomic force microscope (AFM) tips [1,4]. In this work, we focused on metal-coated AFM tips, because the AFM is widely used in research laboratories, suitable for many different samples and can provide different image contrasts. To date, using this type of Ag-coated dielectric tips, TERS measurement has been successfully demonstrated on different samples, such as, carbon nanotubes [5], DNA bases [6], bacterial cell surfaces [7] and fullerene [8].

However, Ag-coated dielectric tips suffer from two severe constraints, namely, the low yield of ‘hot’ tips and their short lifetime. It is known that the optical properties of nanostructures are very sensitive to their shape, size and environments. The low yield of ‘hot’ tip is caused by the

lack of the precise control of those parameters. Recently, Yeo et al. reported [9] that the yield of ‘hot’ tips can be significantly improved by changing the material of the dielectric tip. The authors pointed out that the resonance frequency of localized plasmon of the Ag coating is a function of the refractive index of the dielectric tip. When a proper material is chosen, the resonance frequency of the Ag-coated tip will match the wavelength of the excitation laser and consequently generate a huge Raman enhancement. This hypothesis was also supported by the numerical simulations [10]. Besides the low yield, the short lifetime of the ‘hot’ Ag-coated tips also limits the application of TERS. There are two possible reasons for the fragility of the Ag tip: first, the Ag coating is mechanically fragile [11]. Secondly, Ag is not sufficiently chemically inert. During our experiment, the enhancement fades after half of a day in ambient. It is likely caused by the oxidation of the Ag layer. Moreover, during the measurement, the analytes, especially biomolecules, can easily adsorb onto the Ag tip and caused tip contamination. To overcome these problems, the easiest way is to use a thin robust and inert layer to mechanically sustain the tip apex and shield Ag from the ambient. This has been reported for SERS substrates [12–14]. However, this method has not

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been used for TERS-tip protection so far, because of the following questions: (1) Will the protection layer shift the resonance frequency of the original tip? (2) Can the enhancement be preserved? (3) Will the spatial resolution deteriorate by the size increase of the tip? To answer these questions, we consider two typical chemically inert materials, Au and SiO₂. Full 3D numerical investigations reveal that a thin additional coating layer, which plays an important role for protection purposes, results in only a minor wavelength shift in the optical response of the tip, while still maintaining high field enhancement, provided an appropriate choice of layer material and layer thickness.

In order to have a concise picture of how a protection layer influences the performance of a tip, an equivalent spherical nanoshell structure was investigated first. The shell structure consists of three parts: a SiO₂ core ($n = 1.5$) with a diameter of 10 nm, a middle layer of Ag with a thickness of 25 nm and a protection layer made of Au or SiO₂. Plane wave is used as the excitation source. The wavelength range under investigation is the blue–green area of the visible spectrum. All the known geometrical parameters are adopted from the values of real tips, which have been optimized experimentally [9] and theoretically [10] for tip-enhanced spectroscopy. Benefiting from the simplicity and high symmetry, the scattering problem of these nanoshell structures can be solved by both analytical [15] and numerical methods. Here, we numerically solved the problem with the finite element method (COMSOL multiphysics) [16] in conjunction with a realistic metallic material model [17]. To ensure accuracy in the solution involving vastly differing length scale, adaptive meshing and re-meshing [16] are used to resolve fine features in the model geometry. The mesh is everywhere much finer than the free space wavelength and the final meshes typically resulted in $O(10^6)$ degrees of freedom. The final meshing was adopted until the positions of resonance peaks did not change compared to the previous solutions with different mesh schemes. Scattering boundary conditions and perfectly matched layers integrated in [16] are used together and these boundaries are put at least 500 nm (larger than half of the incident wavelength) away from the calculation domain [10] to achieve high absorption efficiencies.

As can be seen from Fig. 1, a red-shift is obtained for increasing protection layer thickness. For a 10 nm thick Au layer, only a small red-shift of 3 nm is observed (from 495 nm to 498 nm as shown in Fig. 1a), while a 6 nm red-shift is associated with a layer thickness of 20 nm. There is quite good agreement with the analytical solutions for nanoshell [15], and the typical differences for peak positions are hovering around 1%; while for the electric field enhancement, the differences are around 3% (analytical solutions did not show here because of small variations with our results). The comparison with analytical solutions confirms the accuracy of our simulations. Similar results have been obtained from SiO₂ coatings (Fig. 1b). At resonance, the maximal field enhancement for a 10 nm

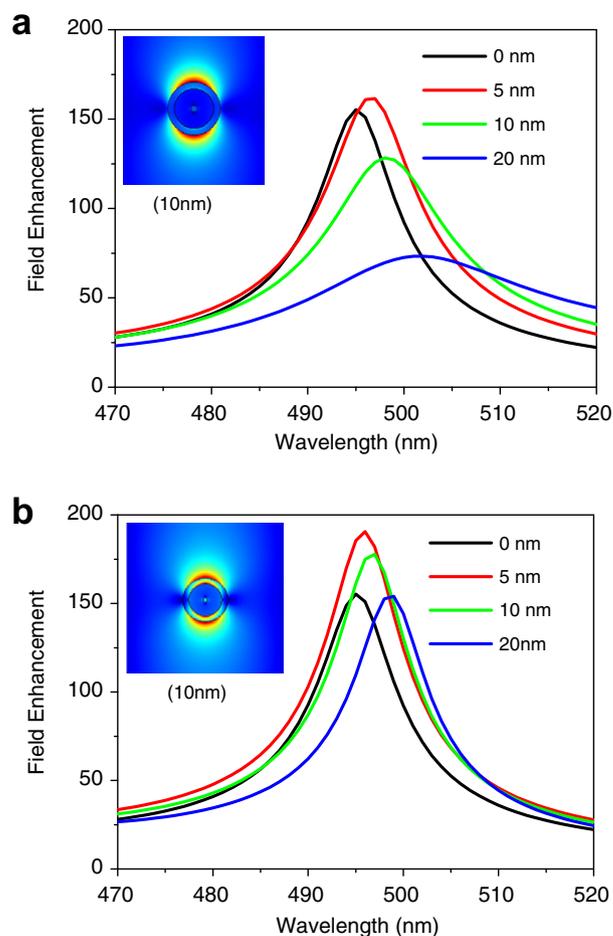


Fig. 1. Three-dimensional simulation of the field enhancement as a function of the incident wavelength for the two-layer nanoshell model. The field enhancement is parameterized with the thickness of the outermost coating layer. (a) The coating layer is Au; (b) the coating layer consists of SiO₂. Inset: field distributions of the localized plasmons at the resonance.

Au protection layer turned out to still be 1.2 times smaller compared to the unprotected nanoshell. This reduction factor will rise to 2.7 if the thickness of the Au is increased to 20 nm. Such behavior can be intuitively understood to originate from the absorption by the additional Au layer. However, it is worth mentioning that nanoshell structures with multiple layers can – if properly designed – provide very large field enhancement factors because of in-phase plasma oscillation interactions [18]. Interestingly, the field enhancement for a 5 nm SiO₂ layer at resonance is larger than for the unprotected case (around 13%) and it remains high values until the thickness up to 20 nm.

Even if the spherical nanoshell model provides an approximative model [19] for the electromagnetic response of the tip, only full 3D models are capable to properly validate the impact of the protective layer on Ag-coated tips. The 3D model of the tip is set up, first, as an inverted dielectric cone with a full-angle of 60° where the tip apex is terminated with a hemisphere having a diameter of about 10 nm. Second, coating layers are assumed to uniformly cover the dielectric surface, and the tip apex end of the

coating layers are concentric with the dielectric tip end, as shown the inset in Fig. 2. Third, the resulting tip geometry was truncated at the height of 520 nm due to computational considerations. A numerical study [20] has demonstrated that the influence of the tip length (i.e., the artificial truncation) on the tip response becomes weaker for decreasing excitation wavelengths, provided these wavelengths are always smaller than the tip length. For realistic tip configurations, the truncation effect may even be neglected although its weak influence on the exact spectral position of the plasmon resonance. Since only the

p-polarization component of electric field (along the tip axis) can be greatly enhanced (unlike the nanoshell calculation because of the structural symmetry) [19,21], a TM mode incident light beam (E is parallel to the tip) was employed for the full 3D simulation.

The full 3D simulation results are shown in Fig. 2. As expected, the basic features of the spectral response are similar to the case of the nanoshell structures. After the tip is coated by a 5 nm SiO_2 layer, the resonance frequency is slightly red shifted by 3 nm and the maximal field enhancement is increased as well about 30% (see Fig. 2). This turned out to be insensitive to the SiO_2 protection layer thicknesses for values up to 10 nm. The high field enhancement caused by the added thin SiO_2 layer is likely attributed to an increased coupling between the plasmons on the inner side of the Ag-layer and the localized surface plasmon on the outer side of this layer [18]. The field distributions for different coatings with respect to their resonances are shown in Fig. 3 for comparison. It is worth mentioning that the field distribution of these plasmon modes is also reproduced by the equivalent nanoshell model in Fig. 1 (including the annotated red-shift). For the Au protected tip, the plasmon modes on the inner and outer bi-metal surfaces are oscillating out of phase, resulting in a significantly lower field enhancement. The associated slight blue shift of the Au protected tip (in Fig. 2) is attributed to the effective change of the dielectric environment and thus affecting the resonance condition. As a comparison, the case for a 20 nm protection layer was also simulated. As in the case of the nanoshell particles, a thicker layer further spoils the field enhancement.

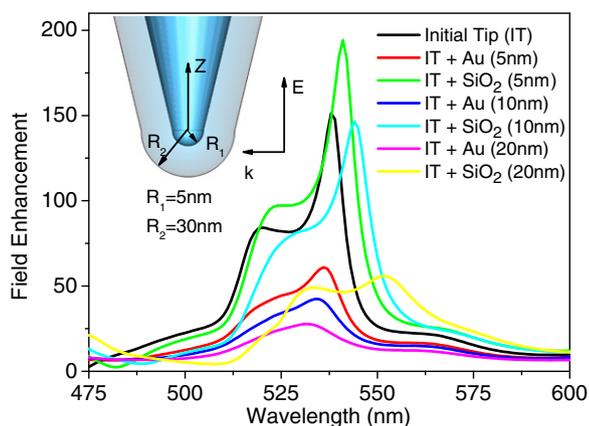


Fig. 2. Full 3D simulations of the overall tip geometry for two different protection coatings. The curves display the field enhancement as a function of incident wavelengths for three cases involving two different protection layer thicknesses. Inset: schematic drawing of a 3D initial conical tip.

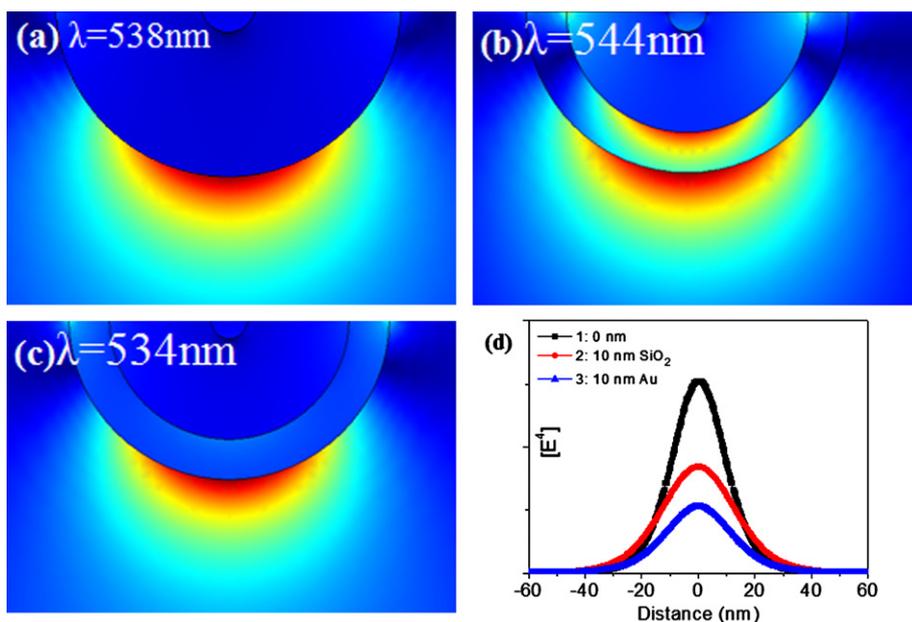


Fig. 3. Resonant field distributions of the axial component $|E_z|$ at the tip apices for different configurations. Vertical cross sections of the 3D tips: (a) for the initial tip at the resonance wavelength of 538 nm; (b) for the tip with a 10 nm SiO_2 protection layer at 544 nm; (c) for the tip with a 10 nm gold protection layer at 534 nm; (d) the fourth power of the electric field strength on a line along the tip apex' boundary (at resonance). The full width at half maximum roughly gives the resolution of the tip for Raman signal. For graphical reason, the scaling of the curves two and three in (d) is amplified 2 and 20 times, respectively.

One of the most important concerns of this protection strategy is that a protective coating layer will increase the size of the tip end and may consequently degrade the spatial resolution of the tip. In order to address this concern, we checked the field distribution of the structure at the resonance frequency shown in Fig. 3 and subsequently plotted the Raman enhancement factor, which is approximated as the fourth power of the field intensity of the field enhancement along the cross section under the tip end (Fig. 3d). The corresponding full width at half maximums (FWHMs) of the plots are calculated. The FWHMs shown in Fig. 3d are 18 nm, 23 nm, 22 nm for the initial tip, the tip with a 10 nm SiO₂ protection layer, and the tip with a 10 nm Au protection layer, respectively. The increment of the FWHMs is much less than the increase of the thickness of the protection layer.

It is worth emphasizing that the proposed tip protection method is feasible, because SiO₂ layers are easily deposited e.g. by vapor coating technique such as PECVD. Experimental work on SiO₂ protection coated samples consisting of Ag island films have already provided SERS signatures without substantial loss in the enhancement factor [14].

To summarize, we have numerically demonstrated that a protection coating maintains or even enhances the functionality of an initial Ag-coated dielectric tip, when an appropriate coating material and layer thickness is chosen (i.e., SiO₂ with 5 nm thickness). More interestingly, the protective coating does not greatly affect the spatial resolution of the tip although the tip radius is increased by 20 nm. Considering the success of applying protecting layers in SERS, the approach we propose here might be an effective method to produce robust TERS tips. We are therefore looking forward to experimental verifications, which are scheduled for the near future.

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